

## Conference Paper

# Extraction Recovery of Vanadium(V) by Amines

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## Abstract

The extraction of vanadium (V) by N-(2-hydroxy-5-nonylbenzyl)- $\beta$ ,  $\beta$ -dihydroxyethylamine was studied depending on different factors, such as pH of the medium, concentration of extracting agent, temperature and solvent type. This allowed the optimal extraction conditions to be determined. It was shown that extraction of vanadium (V) takes place with high distribution coefficients, and a complex containing a decavanadate anion and four molecules of the extractant is formed in the organic phase. The extracted vanadium (V) complex with amine is stable for more than one month.

**Keywords:** extraction, vanadium, distribution coefficient, infrared spectroscopy.

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Published: 31 December 2020

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Analysis of available technologies for vanadium recovery shows that neither of them meets in full measure the modern product quality, metal extraction completeness and ecological cleanliness requirements. Efficient ecologically sound processing of vanadium-containing raw materials can be realized only on the basis of comprehensive physicochemical studies of all stages of pyro- and hydrometallurgical processes.

The most effective method for vanadium recovery from process liquors at the stage of hydrometallurgical processing of vanadium-containing feedstock is extraction. Extraction is one of the most promising techniques for producing high-purity vanadium compounds. Extraction processes have some advantages over sorption, deposition and other purification and separation processes. They are highly efficient, can be easily automated and permit the creation of continuous flowcharts, which makes it possible to develop environmentally sound processes. In the world practice vanadium is usually extracted from acid solutions. So, neutral extractants (tributyl phosphate, alcohols) recover vanadium in the oxidation state five from concentrated solutions of hydrochloric acid. However, their application is not effective enough since in concentrated solutions of hydrochloric acid co-extraction of hydrochloric acid and reduction of vanadium (V) to vanadium (IV) can take place. This decreases the degree of vanadium (V) extraction.

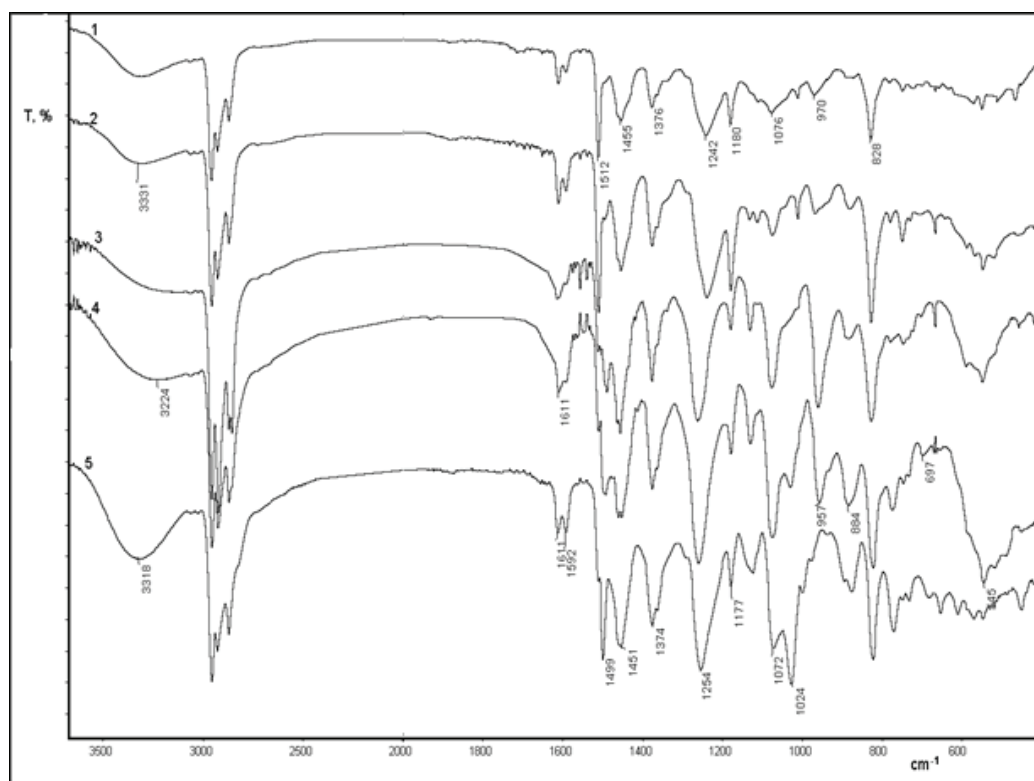
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Di-2-ethylhexylphosphoric acid is a cation-exchange extracting agent, which is used in technology only for extraction of vanadium in the oxidation state four [1, 2]. Its application for the extraction of vanadium (IV) also involves some difficulties. In the process solutions, vanadium has usually the oxidation state five and for its extraction by di-2-ethylhexylphosphoric acid a preliminary stage of vanadium (V) reduction to vanadium (IV) is required in the flowchart. Besides, vanadium (IV) can be oxidized by atmospheric oxygen, therefore in order to reduce losses into the ambient medium during vanadium (IV) extraction by di-2-ethylhexylphosphoric acid, an inert or reducing atmosphere is needed. Note that extraction of vanadium (IV) by di-2-ethylhexylphosphoric acid occurs with a low distribution coefficient ( $K_{V(IV)} = 6-8$ ). That is why extraction of vanadium (IV) requires at least six stages of extraction. With that in mind, finding of an available extractant providing vanadium extraction with high distribution coefficients is a topical problem. In this work we present the results of investigation of vanadium (V) extraction from subacid solutions by phenol-type amine N-(2-hydroxy-5-nonylbenzyl)- $\beta$ ,  $\beta$ -dihydroxyethylamine (NBEA).

The extraction of vanadium (V) by phenol-type amine N-(2-hydroxy-5-nonylbenzyl)- $\beta$ ,  $\beta$ -dihydroxyethylamine was examined. The effect of different factors (pH of the environment, vanadium (V) concentration, extractant concentration, temperature, type of solvent) on the extraction of vanadium (V) was studied. The studies performed revealed that extraction of vanadium (V) by phenol-type amine should be carried out in a subacid region. As follows from the examination of the ionic state of vanadium (V) performed earlier as a function of its concentration and pH of solution, it exists in a subacid region in the form of diprotonated decavanadate anion  $H_2V_{10}O_{28}^{4-}$  [3]. To confirm this conclusion, the aqueous solution of vanadium (V), from which extraction was performed, was studied by the NMR spectroscopy method. Three lines at -420, -510 and -590 ppm were found in the  $^{51}V$  NMR spectra, which according to [4] suggests the existence of vanadium (V) in the subacid solution in the form of diprotonated decavanadate anion  $H_2V_{10}O_{28}^{4-}$ . This allows one to suppose that in the subacid region phenol-type amine extracts vanadium (V) in the anionic form as a diprotonated decavanadate anion  $H_2V_{10}O_{28}^{4-}$ . In the  $^{51}V$  NMR spectrum of the organic phase, line broadening and a high-frequency shift to the region of -491 and -521 ppm are observed suggesting the formation of a complex compounds of vanadium (V) with N-(2-hydroxy-5-nonylbenzyl)- $\beta$ ,  $\beta$  dihydroxyethylamine. The extracted complex compound of vanadium (V) with amine was studied with the use of infrared and electron spectroscopy methods.

The infrared spectra of vanadium (V) extracts by NBEA were found to contain the bands of stretching vibrations of free vanadium-oxygen bonds at  $960\text{ cm}^{-1}$  and bridge bonds V-O-V at  $750$  and  $590\text{ cm}^{-1}$ , which, according to [5], can be attributed to

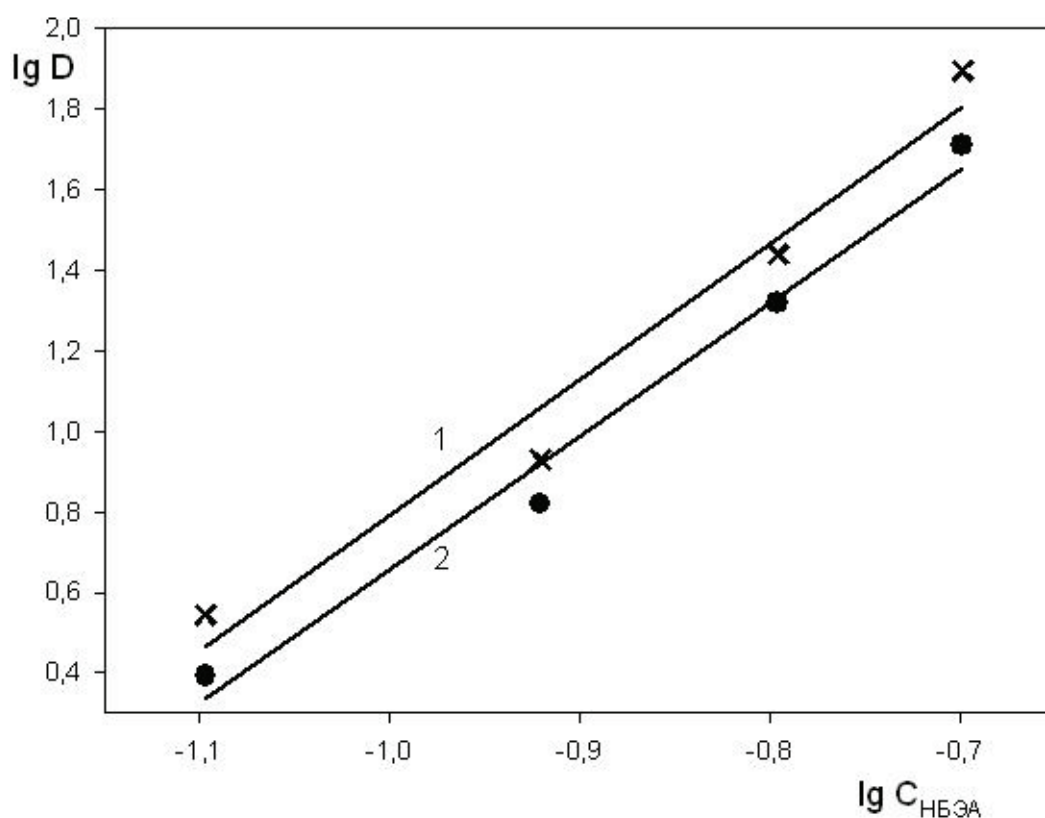
vibrations of V-O bonds in decavanadate anion. (Figure 1). Besides, during extraction of vanadium (V) in the subacid region (pH=3.6) changes are observed in the shape and redistribution of intensities of N-(2-hydroxy-5-nonylbenzyl)- $\beta$ ,  $\beta$



**Figure 1:** The infrared spectra of vanadium(V) extracts by NBEA. 1 – NBEA; 2 – pH=3.73; 3 – pH=3.61; 4 – pH=3.08; 5 – pH=2.60.

dihydroxyethylamine bands relating to vibrations of O-H and C-N bonds in the region of 1020-1100, 1255-1262  $\text{cm}^{-1}$ , as well as to vibrations of benzene ring: the bands at 1514 and 1609 strengthen and the band at 1495  $\text{cm}^{-1}$  decreases. Apparently, the complex of decavanadate anion with NBEA is formed not only by the interaction of vanadium with nitrogen and oxygen of hydroxyl groups, but also with the electronic structure of benzene ring. Note that in the region of stretching vibrations of O-H bonds, broad absorption appears in the interval 3590 - 2300  $\text{cm}^{-1}$ , and a weak band appears at 1720  $\text{cm}^{-1}$ , which may be indicative of the formation of a strong hydrogen bond. As pH decreases to 2.97, the band at 1495  $\text{cm}^{-1}$  disappears almost completely and the shape of the bands at 1262 and 1070  $\text{cm}^{-1}$  changes further, which may point to the formation of a stronger complex of vanadium (V) with phenol-type amine.

To determine the quantity of extractant molecules entering into the composition of extracted complex, the extraction of vanadium was studied as a function of extractant concentration at constant pH and constant vanadium (V) concentration in solution (Figure 2). Analysis of the dependence of the



**Figure 2:** The distribution coefficient of vanadium(V) versus the concentration of NBEA. 1 – pH= 2.1; 2 – pH=3.0.

vanadium (V) distribution coefficient on the concentration of extractant shows that the slope of the logarithmic dependence of the distribution coefficient on the extractant concentration is four. Based on these data and the fact that vanadium (V) in subacid solutions is in the form of diprotonated decavanadate anion  $H_2V_{10}O_{28}^{4-}$  [4], its extraction by amine takes place with the formation of a complex containing diprotonated decavanadate anion  $H_2V_{10}O_{28}^{4-}$  and four extractant molecules.

The stability of vanadium (V) complex extracted by amine was studied by means of electron and infrared spectroscopy methods. It was found that the electronic spectrum of the extracted vanadium (V) complex with NBEA contains no bands typical of vanadium (IV) oxocation in the region of 600-700 nm [1]. The extracted complex of vanadium (V) with amine is stable for more than one month and is not reduced. The results obtained are also confirmed by the infrared spectroscopy method. Analysis of the infrared spectra of vanadium (V) extracts by phenol-type amine reveals that no reduction of vanadium takes place in the organic phase in the course of time. In the infrared spectra of as-prepared vanadium (V) extracts by NBEA and also in the spectra of a sample prepared more than a month ago, we have detected the bands of stretching

vibrations of free vanadium-oxygen bonds at  $960\text{ cm}^{-1}$  and bridge bonds V-O-V at  $750$  and  $590\text{ cm}^{-1}$ , which, as shown above [5], are related to vibrations of V-O bonds in decavanadate anion. We did not find any bands typical of vanadium (IV) oxocation in the region of  $1000\text{ nm}$  [6]. The studies performed demonstrate that the extracted complex of vanadium (V) with amine is stable for more than one month and is not reduced, which is of great importance for technology, especially when choosing extraction and re-extraction conditions.

The effect of temperature on the extraction by phenol-type amine was examined at a high concentration of vanadium (V) in the initial solution. The studies showed that an increase in temperature to  $50\text{ }^{\circ}\text{C}$  and temperature reduction to zero do not change the vanadium (V) distribution coefficient by phenol-type amine. Temperature is likely to have no effect on vanadium (V) extraction by phenol-type amine. With this consideration in mind, extraction was carried out at  $25\text{ }^{\circ}\text{C}$ .

It is known that amine salts in low-polarity and non-polar solvents have limited solubility [7]. To increase the solubility of amine salts, their salvation by polar solvents is employed. Alcohols are usually used as a solubilizing addition to amines. In this connection we used octanol as a solubilizing agent.

## 1. Conclusions

Our study of vanadium (V) extraction by phenol-type amine showed that under optimal conditions phenol-type amine extracts vanadium (V) with high distribution coefficients ( $\lg D \geq 2$ ). A stable complex of vanadium (V) with amine is formed. This allows us to recommend N-(2-hydroxy-5-nonylbenzyl)- $\beta$ ,  $\beta$  dihydroxyethylamine as an effective extractant of vanadium from subacid solutions.

*The work was performed in accordance with the state assignment and R&D plans for ISSC UB RAS.*

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